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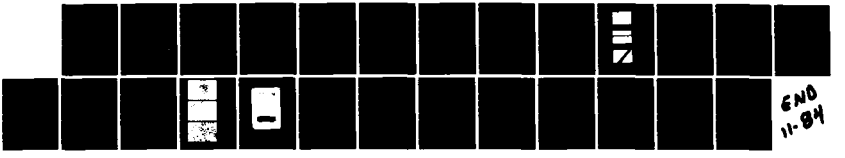

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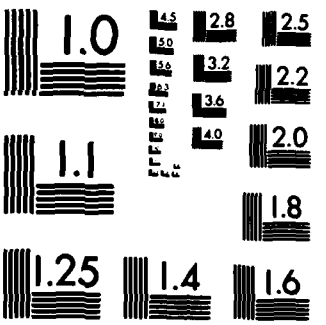

ELECTRONIC TRANSPORT PROCESSES IN REFRACTORY METAL SILICIDES

FINAL REPORT

J. E. Mahan

Department of Electrical Engineering and
Condensed Matter Sciences Laboratory
Colorado State University
Fort Collins, CO 80523

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refractory metal silicides, transport properties, metallization, interconnects, gate electrode material

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The electronic transport properties of $TiSi_2$, $TaSi_2$, $MoSi_2$, and WSi_2 thin films were investigated. The films were prepared by neutralized ion beam sputtering of the metals onto silicon surfaces, followed by furnace reaction in an inert atmosphere to form the disilicide film. X-ray

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diffaction and Auger analysis indicate that single-phase disilicide films were obtained, with no detectable impurity content. The residual and intrinsic resistivity components were determined. Hall effect and magnetoresistance measurements were made to determine the dominant carrier type and obtain representative mobility estimates. It was found that multicarrier effects prevail in all of the materials.

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II. STATEMENT OF THE PROBLEM STUDIED

The electrical and chemical properties of certain refractory metal silicides make them attractive as materials for improved interconnection lines and gate electrodes in silicon integrated circuits. The potential for reduced RC time constants and therefore reduced access time in VLSI memory chips has stimulated a number of current silicide research programs in government, university, and industrial laboratories. The resistivity of the silicide can be an order of magnitude lower than that of the most conductive polycrystalline silicon interconnection material in present use, and is occasionally lower than that of the pure refractory metal itself. In addition, certain refractory metal silicides have been found to be compatible with the wet and dry chemistry of existing LSI technology; they have shown the ability to grow a native silicon dioxide layer under conditions similar to those appropriate for polycrystalline silicon films, which the pure refractory metals cannot do.

Most refractory metal silicide phases are reported to be metallic conductors, based on measured resistivities in the 10-100 μΩ-cm range. Beyond this, high quality data on the transport properties is scarce. There is little information regarding the nature of electronic transport processes in these materials. Some data on the transport properties of a few silicides do exist, but the studies are often 15-20 years old and are of questionable validity. In many cases the studies were based on bulk samples made by sintering the constituent elements in a furnace; a number of impurity-stabilized tertiary compounds were mistakenly identified as stable silicides. The high purity thin film preparation techniques of the microelectronics field were not available when these studies were conducted.

In order to make informed choices regarding the selection of these materials for use in electronic devices, a fundamental understanding of electronic

transport has been needed. There are a number of important questions: What is the dominant charge carrier type, density, and mobility? What are the physical mechanisms underlying annealing-induced resistivity changes? What are the effects of impurity atoms on the structure and electrical properties of the silicides? What is the nature and distribution in energy of the allowed electron states in the vicinity of Fermi level? What is the intrinsic resistivity and what are the possible scattering mechanisms contributing to any residual resistivity? Why are the disilicides apparently the best conductors? What are the effects of the presence of multiple phases within a refractory metal silicide thin film? How can the material properties be tailored for specific purposes through controlled microstructural modifications?

This research was an investigation of the physics of electronic transport in refractory metal silicide thin films, with primary emphasis on the titanium, tantalum, and tungsten disilicides. Experimental characterization of $MoSi_2$ and semiconducting $FeSi_2$ thin films is being completed at the time of writing this report. Thin films of the metals were deposited by neutralized ion beam sputtering from high purity targets onto silicon wafers. The metal films were subjected to annealing treatments to induce silicide formation. Structural and compositional characterization were done using techniques of X-ray diffraction, scanning electron microscopy, and Auger/ESCA spectroscopy.

The electronic transport properties of the silicide layers were determined through detailed measurements of resistivity, Hall coefficient, and geometrical magnetoresistance and their temperature dependences. From the transport data obtained an initial picture of electronic transport processes in refractory metal silicide thin films was formulated.

III. SUMMARY OF RESULTS

Single phase disilicide films were obtained by depositing about 1000Å of the metal onto a polycrystalline silicon (polysilicon) surface (or in some cases onto a bare polished wafer ion milled in vacuo before metal deposition). The diffusion couple was reacted in an argon atmosphere within a quartz tube furnace. This approach relies on the natural tendency, with excess silicon present, to totally consume the metal layer in forming the disilicide phase. Selected examples of SEM fracture cross sections showing an as-deposited titanium film and a furnace-reacted WSi_2 layer on polysilicon and a $TaSi_2$ layer formed on a bare wafer are shown in Figure 1.

The sharp peaks in the X-ray diffraction pattern for a representative $TaSi_2$ film shown in Figure 2 indicate the film is very well crystallized; there is a nearly random texture, and a total absence of peaks not attributable to $TaSi_2$ or to the substrate. Auger analysis of the three disilicides showed very high surface concentrations of carbon and oxygen as one would expect, but these reduced to trace levels upon ion milling within the Auger analysis chamber. There were no other detectable impurities within the interior of the films. A representative Auger spectrum for WSi_2 is shown in Figure 3, obtained after milling for 15 minutes.

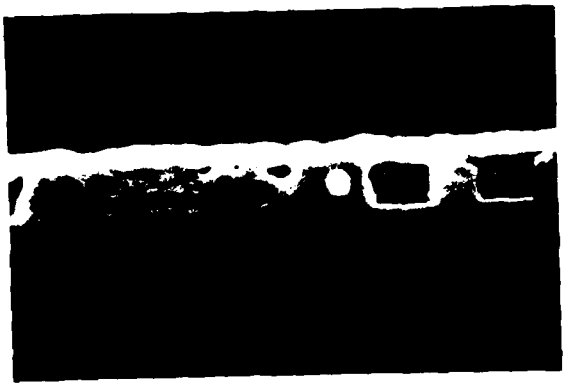
As will be discussed in the next section, residual and intrinsic resistivity contributions for these films were estimated. The size of the residual resistivity is a measure of the amount of imperfections present in a metal; while our residual resistivity ratios ($\rho(273K)/\rho(0)$) were on the order of ~1/1, many pure metals have been prepared having residual resistivity ratios of several hundred. From this perspective the films must be considered quite defective; however, the resistivities observed are at least equal to the lowest values reported in the literature for these materials in thin film form.

1000 Å Ti

4000 Å polysilicon

1000 Å SiO_2

Si wafer

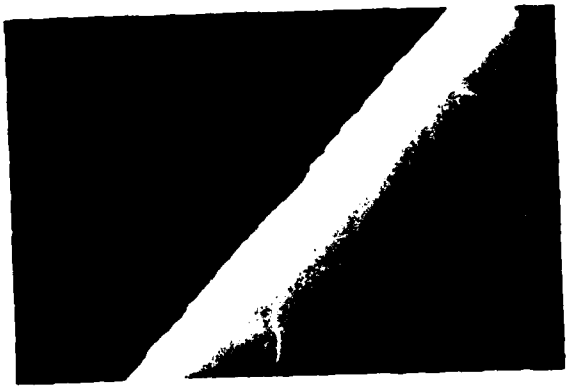


2000 Å WSi_2

8000 Å polysilicon

10,000 Å SiO_2

Si wafer



2000 Å $TaSi_2$

Si wafer

Figure 1.

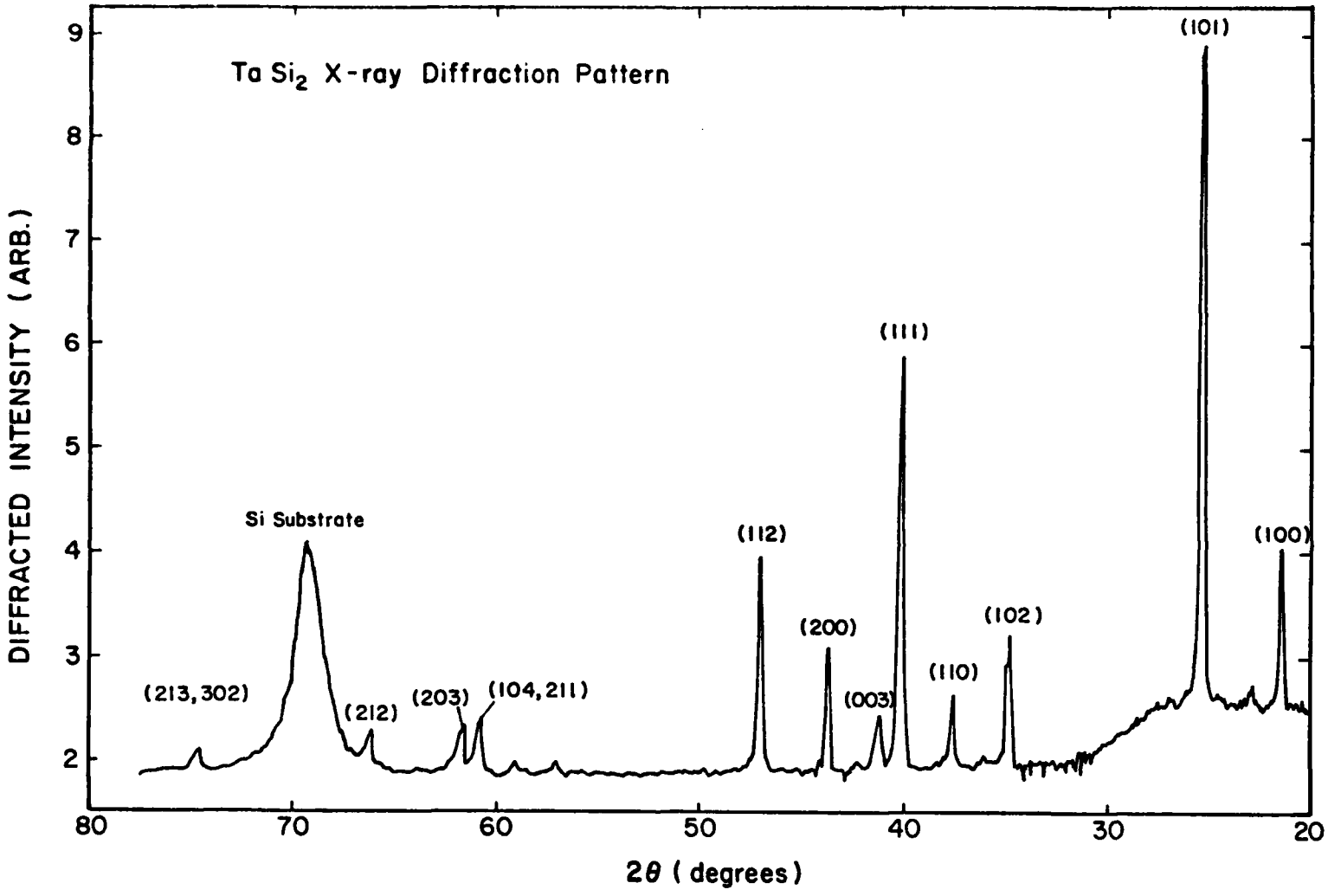

Ta Si2 X-ray Diffraction Pattern
DIFFRACTED INTENSITY (ARB.)
2θ (degrees)
Si Substrate
(213,302)
(212)
(203)
(104,211)
(112)
(200)
(003)
(111)
(110)
(102)
(101)
(100)
9
8
7
6
5
4
3
2
80
70
60
50
40
30
20

Figure 2

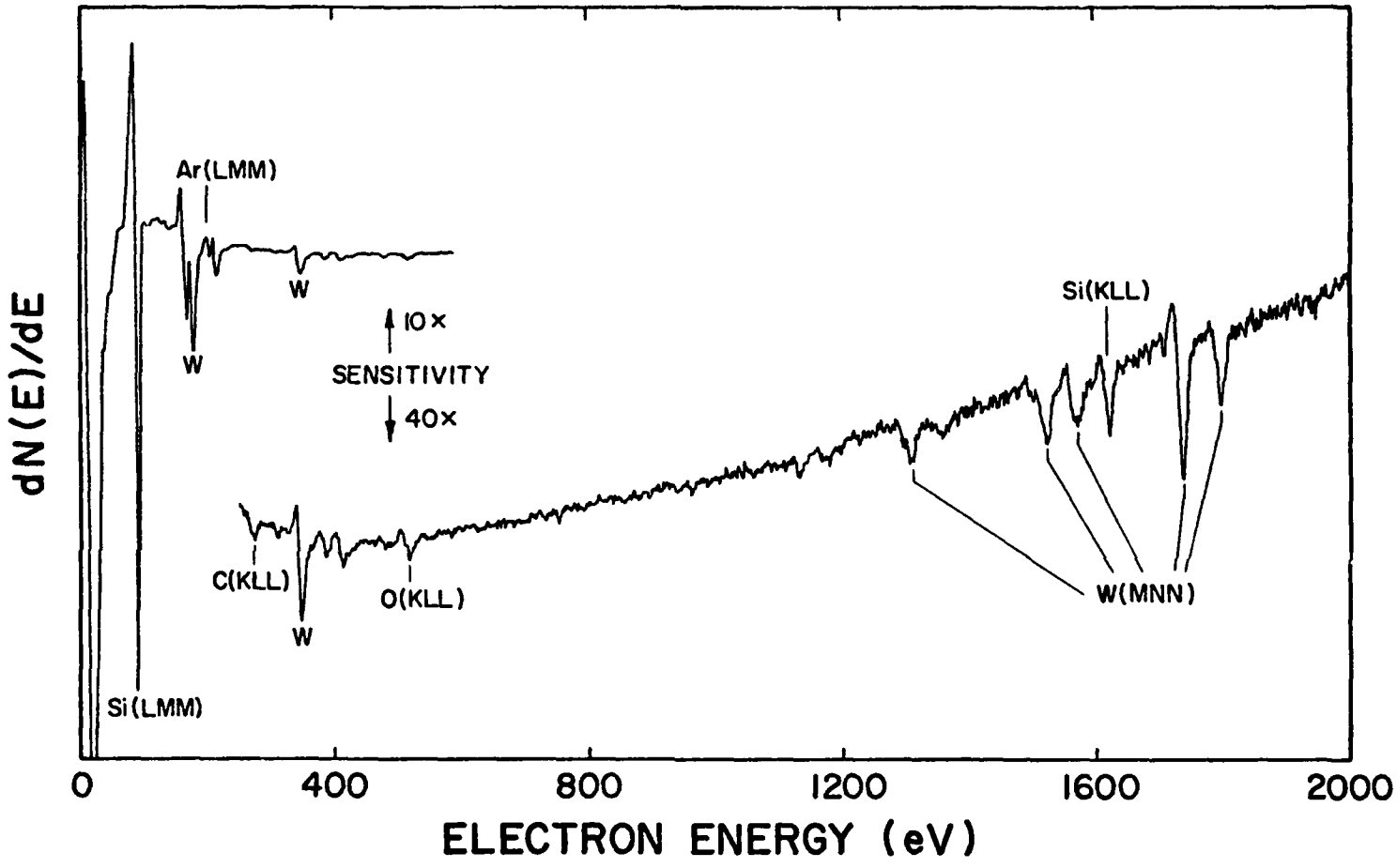

dN(E)/dE
Ar(LMM)
W
W
10×
SENSITIVITY
40×
Si(KLL)
C(KLL)
W
O(KLL)
W(MNN)
Si(LMM)
0
400
800
1200
1600
2000
ELECTRON ENERGY (eV)

Figure 3

Transport Properties

The resistivities as functions of temperature for the three disilicides formed on polysilicon and for $TaSi_2$ on the single crystal substrate as well are shown in Figure 4. The materials resemble classical metallic conductors, with a temperature-independent residual resistivity and an intrinsic resistivity basically proportional to temperature over the range of our measurements. The two resistivity components have been estimated from the data and are given in Table I. The residual resistivity estimates for $TiSi_2$ and WSi_2 are obvious from Figure 4, but that for $TaSi_2$ is not. It was obtained in the process of fitting the classical Bloch-Gruneisen Equation to the data:

$$\rho_i = 4(T/\Theta_R)^5 \rho_\Theta \int_0^{\Theta_R/T} \left[x^5 e^x/(e^x-1)^2\right]dx, \qquad (1)$$

where ρ_i is the intrinsic resistivity, T is the absolute temperature, Θ_R is the Debye temperature, and ρ_Θ is a material parameter depending on the number of "free" carriers and the crystal structure. The calculated curves are shown in Figure 4, translated by an amount equal to the residual resistivity, and the Debye temperatures thus determined are given in Table I. It appears that the lattice vibrational spectrum of $TaSi_2$ is characterized by an atypically low Debye temperature.

We have calculated the intrinsic resistivities in Table I simply by subtracting the residual resistivities from the room temperature total resistivities; the validity of this procedure is supported by the $TaSi_2$ data; the two types of $TaSi_2$ films in Figure 4 have different residual resistivities but apparently the same intrinsic components. There is no detectable difference in impurity content of the $TaSi_2$ films by Auger anaysis, but X-ray diffraction indicates a different grain orientation distribution.

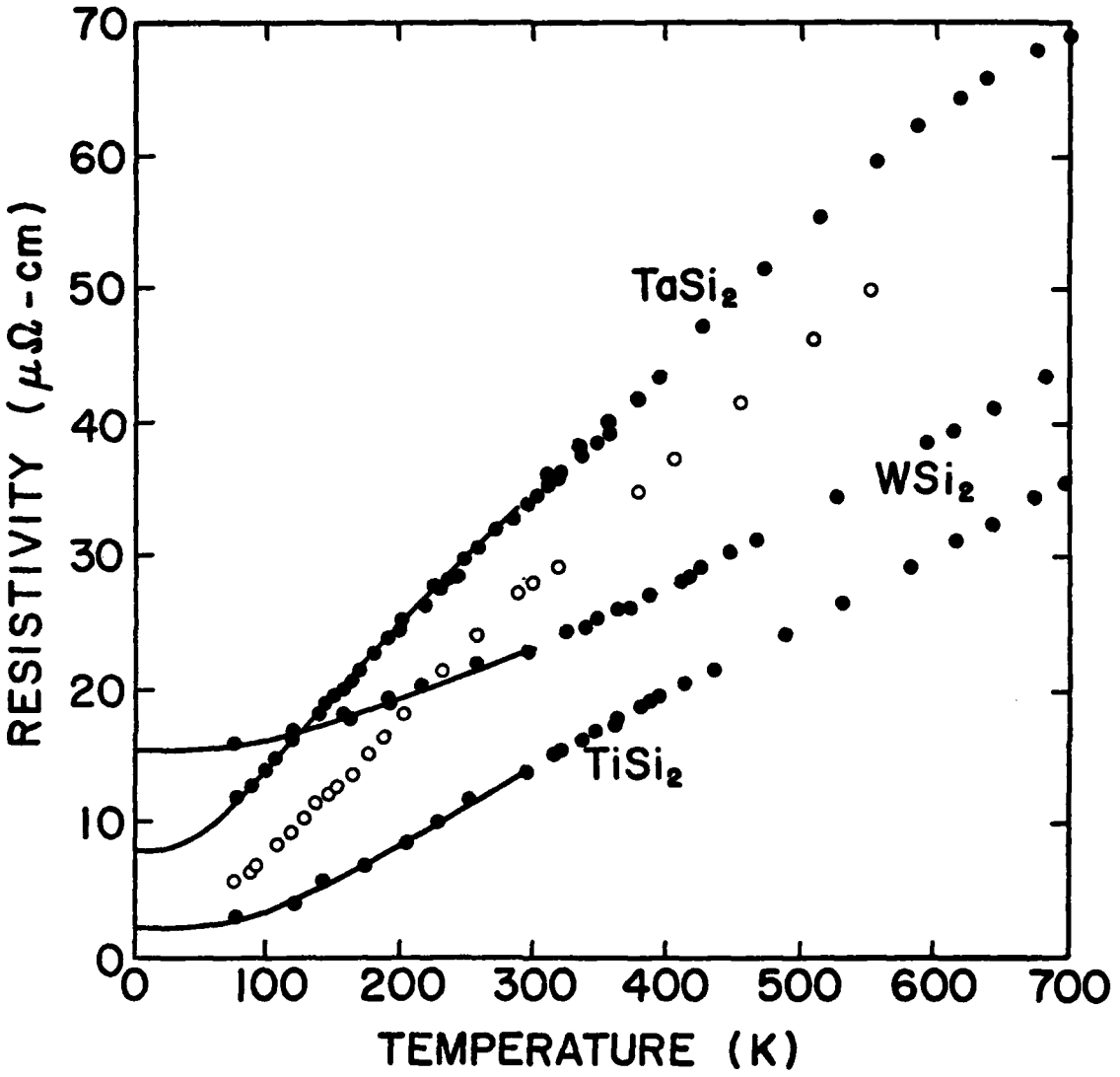


Figure 4. • polysilicon substrate; o bare wafer.

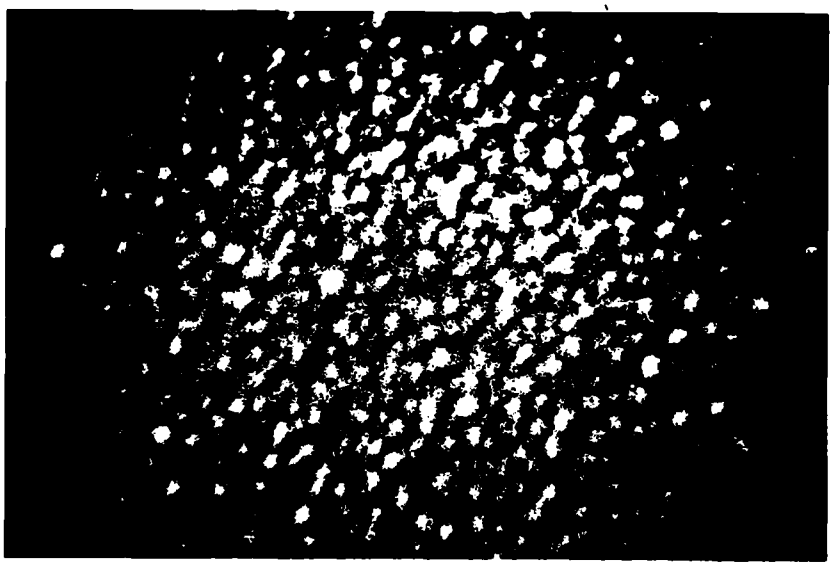
TABLE I

RESISTIVITY PARAMETERS FOR SILICIDES ON POLYSILICON

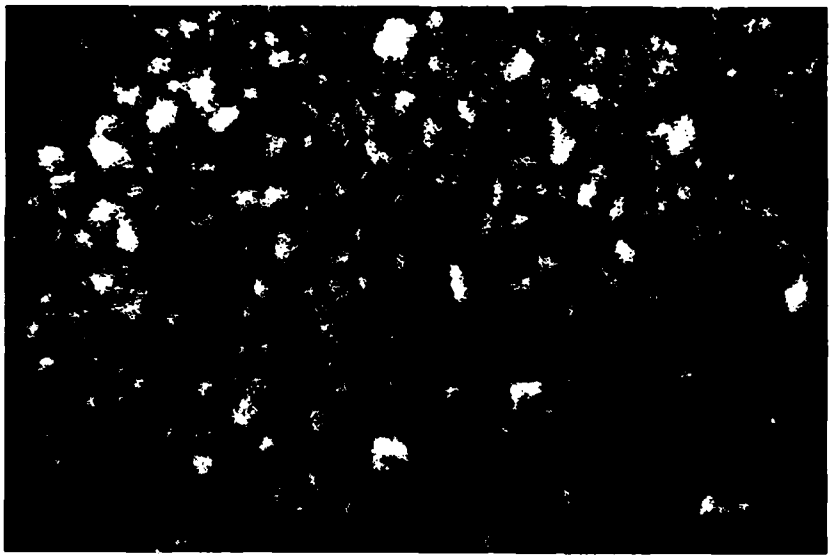
	Residual Resistivity	Room Temperature Intrinsic Resistivity	Debye Temperature
$TiSi_2$	3μΩ-cm	11μΩ-cm	550K
$TaSi_2$	8	26	300
WSi_2	16	7	580
$MoSi_2$	~30	~20	~500

$MoSi_2$ films were also prepared on both substrate types. In contrast to $TaSi_2$, a lower residual resistivity component was obtained with the polysilicon substrate (~30 vs. ~90 μΩ-cm for the bare wafer substrate). SEM surface examination (shown in Figure 5) of the as-deposited molybdenum layer and the two silicide types is very suggestive of grain size differences for the three films that may be correlated with the residual resistivities. There are no detectable differences (by Auger spectroscopy) in impurity content among the sample (in fact, no Auger-detectable impurities at all within the interiors of the films). Although the physical origin of the residual resistivities has not been positively identified for any of the silicide materials we have studied, this recent examination of the $MoSi_2$ samples points for the first time to grain boundary scattering.

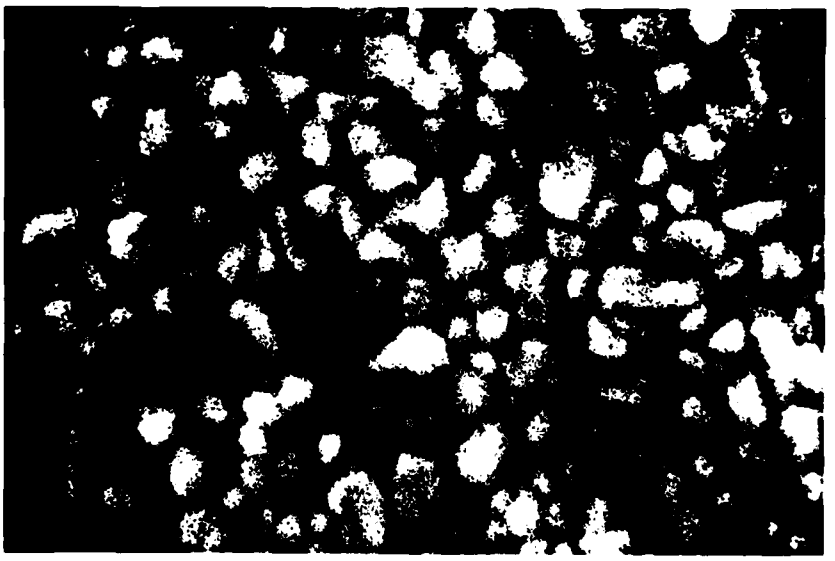
We have found transverse magnetoresistance measurements to be useful in understanding the transport properties of silicide thin films. The transverse magnetoresistance is the fractional change in resistance due to a magnetic field applied normal to the plane of the thin film sample. The geometrical magnetoresistance is observed in a sample prepared in such a manner that the electrical contacts short out the Hall field. The classical form is the Corbino disc. A photomicrograph of a sample with electrodes equivalent to those of the Corbino disc is shown in Figure 6a. The aluminum contacts were patterned photolithographically. The sample was mounted in a hybrid plug-in package (which is standard for all our properties measurements) and double wirebonded to make electrical connections with minimal series resistance effects. Some representative data for $TaSi_2$ at room and liquid nitrogen temperatures are shown in Figure 7. In the two-band, isotropic model, the geometrical magnetoresistance ($(\Delta\rho/\rho_o)_c$) is given by



(a) as-deposited molybdenum

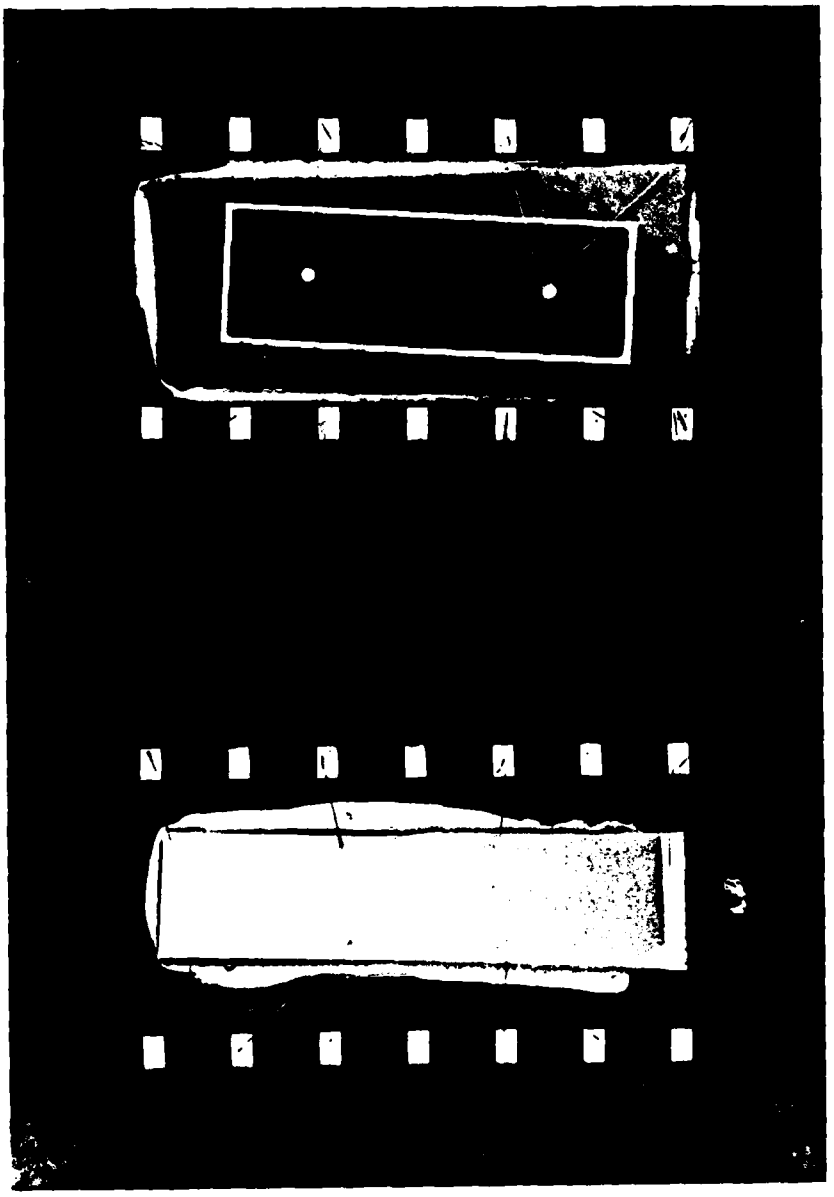


(b) $MoSi_2$ on bare wafer



(c) $MoSi_2$ on polysilicon

Figure 5



(a)

(b)

Figure 6.

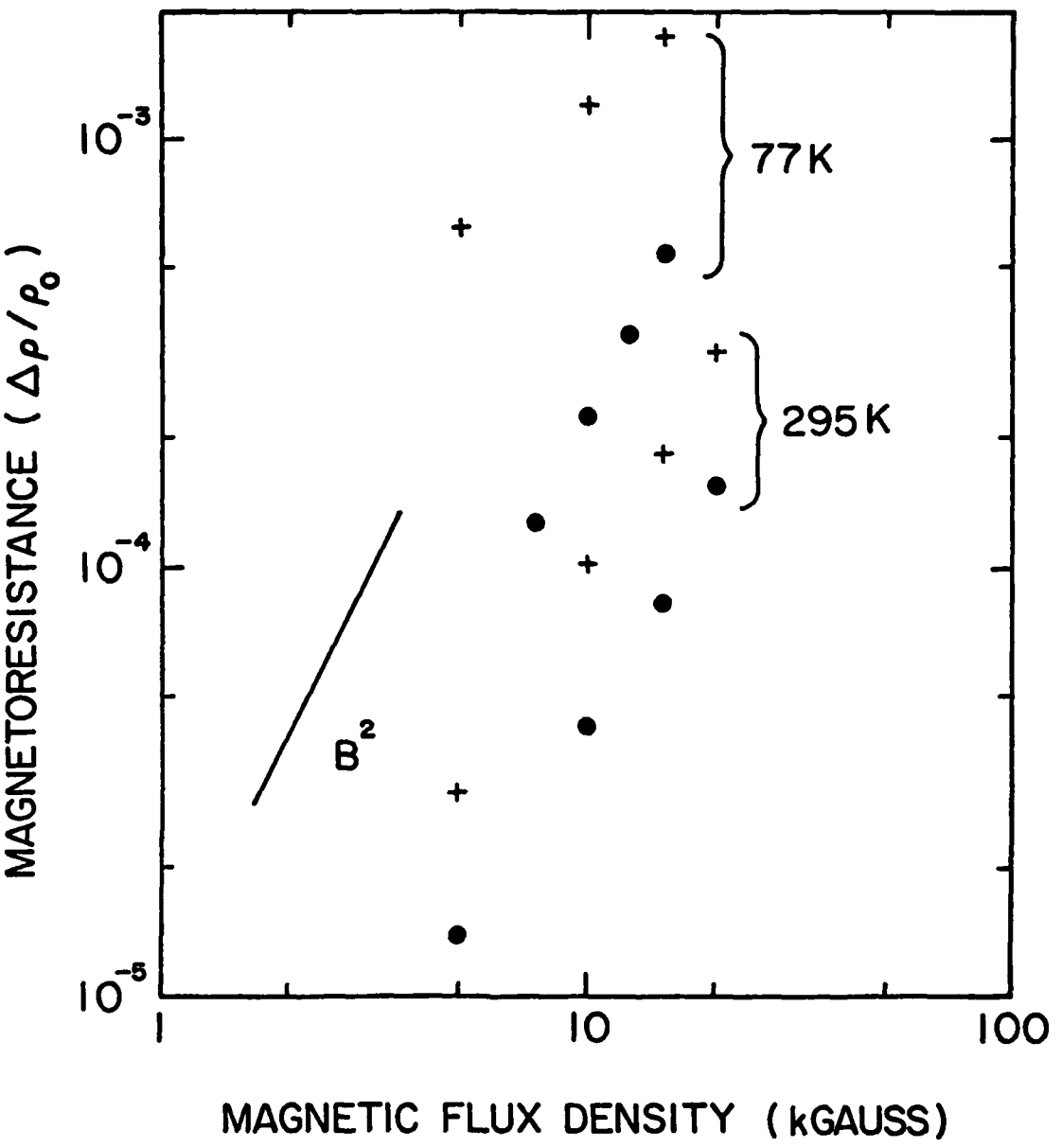


Figure 7. ● polysilicon substrate; + bare wafer.

$$(\Delta\rho/\rho_o)_c = \frac{[\mu_e^2\sigma_e/(\sigma_e + \sigma_h) + \mu_h^2\sigma_h/(\sigma_e + \sigma_h)]B^2 + (\mu_e\mu_h B^2)^2}{1 + B^2[\mu_e^2\sigma_h/(\sigma_e + \sigma_h) + \mu_h^2\sigma_e/(\sigma_e + \sigma_h)]}, \quad (2)$$

where μ_e and μ_h are the carrier mobilities of the two bands, σ_e and σ_h their conductivities, σ_o the total zero-field conductivity, and B the magnetic flux density. Equation (2) predicts a quadratic dependence on B at low fields and, depending on the individual parameters of the two bands, there is the possibility of dropping below the B^2 curve and even a return to quadratic behavior at very high fields. Quadratic behavior was always observed for $TiSi_2$, $TaSi_2$, and WSi_2 on polysilicon, but for $TaSi_2$ on a bare wafer at 77K, the dependence is less than quadratic - this was the only instance and it coincides with some of the largest magnetoresistance values we observed in any sample. This anomalous behavior is due to current flow in the single crystal substrate, which effectively establishes two-band conduction in the sample as a whole. For low fields, Equation (1) reduces to

$$\Delta\rho/\rho_o = (p\mu_h^3 + n\mu_e^3)B^2/(p\mu_h + n\mu_e), \quad (3)$$

and for a single electron band, we have

$$\Delta\rho/\rho_o = (\mu_e B)^2. \quad (4)$$

We have used Equation (4) to calculate what we call the "magnetoresistance mobility," as though there were a single, isotropic band of charge carriers. The results are shown in Table II, for the disilicides formed on polysilicon. For $TaSi_2$, there is a reasonable correlation between the temperature dependence of resistivity and that of the magnetoresistance mobility. Both change by a factor of ~2.6 in going between room and liquid nitrogen temperatures. For $TiSi_2$, the factor is ~4.5 and for $MoSi_2$, ~1.5. For WSi_2, on the other hand, the mobility varies much more rapidly with temperature than one would expect from the resistivity data. This might be interpreted as a shift in the mix of free electrons and holes with temperature.

TABLE II

GALVANOMAGNETIC PROPERTIES OF SILICIDES ON POLYSILICON

	$TaSi_2$	$TiSi_2$	WSi_2	$MoSi_2$
Magnetoresistance mobility 295K:	61 $cm^2/V\text{-}s$	63	95	100
77K:	160	270	230	150
Hall constant (295K)	-6×10^{-5} cm^3/C	-1.5×10^{-5}	$+7.0 \times 10^{-4}$	$+1.3 \times 10^{-3}$
Apparent carrier concentration (295K)	1×10^{23} cm^3	4×10^{23}	9×10^{21}	5×10^{21}
Hall mobility (295K)	1.8 $cm^2/V\text{-}s$	1.0	30	29

The Hall effect in these materials is very small, with Hall voltages on the order of microvolts for a nondestructive current density and reasonable sample size and a magnetic flux density of over 10 kGauss. A $TaSi_2$ Hall sample, mounted and wirebonded into its hybrid plug-in package, is shown in Figure 6b. The results are also given in Table II. $TiSi_2$ and $TaSi_2$ on polysilicon are quite similar, both being predominantly electron conductors with small Hall mobilities and very large apparent carrier densities. $MoSi_2$ and WSi_2 are predominantly hole conductors, exhibiting a Hall effect larger than that of the other materials by over an order of magnitude. There are also significant differences between the two forms of $TaSi_2$. Unusual low temperature behavior again was observed in the $TaSi_2$ films formed on a bare wafer: the Hall voltage saturates as a function of magnetic flux density at values above ~10 kGauss. All of these high field effects are due to current flow in the silicon substrate and do not have their origin in the properties of $TaSi_2$.

It is well known that in cases of mixed conduction the carrier density calculated from the Hall coefficient will be an overestimate of the total carrier density, and likewise the Hall mobility from will be an underestimate of the average carrier mobility. Such appears to be the case for these materials: for $TiSi_2$ and $TaSi_2$, the two room temperature mobility estimates in Table III differ by factors of forty and sixty, while for $MoSi_2$ and WSi_2, the mobility values differ by a factor of three. We take this as clear evidence of mixed conduction, with the effect being the smallest in the column VIA materials. The magnetoresistance-derived mobility value is more nearly representative than the Hall mobility because in the two-band model it is at least bounded by μ_e and μ_h while the Hall mobility may be much lower than either.

We have also investiated in some depth the optical properties of semiconducting $FeSi_2$ thin films. Semiconducting silicides may provide a new basis for

forming infrared detection devices within the planar silicon technology, a need which has been inadequately satisfied to date by detectors based on extrinsic photoconductivity in doped silicon or internal photoemission at Schottky barriers.

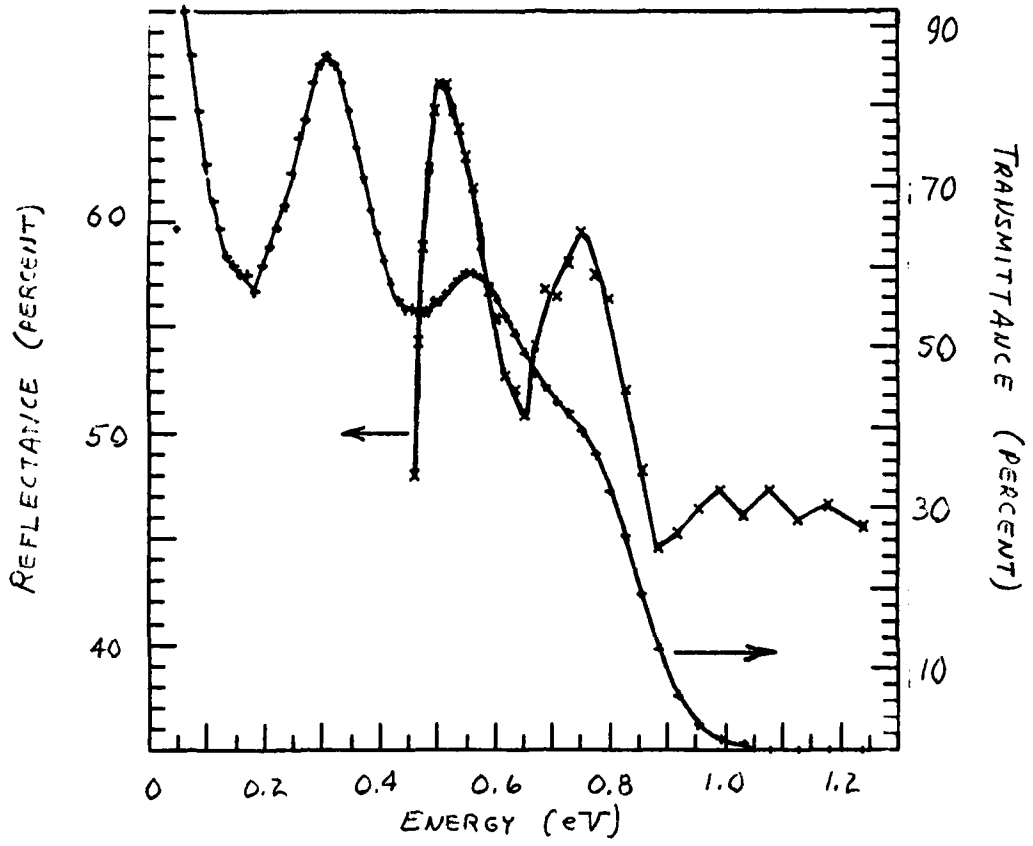
The β-$FeSi_2$ phase has been known for some twenty years to possess a forbidden energy gap of ~0.8 - 1.0eV, as determined from the temperature dependence of intrinsic resistivity and the Hall coefficient. To our knowledge, however, the optical absorption edge or the nature of the forbidden gap have not been determined previously. Such information is essential in assessing optolectronic device potential.

Figure 8a shows spectral transmission and reflection measurements for β-$FeSi_2$ films formed on polished silicon wafers. From these data, the complex index of refraction and thence the optical absorption coefficient were calculated using a computer model. The optical absorption coefficient, shown in Figure 8b, suggests there may be <u>two</u> absorption edges, one at ~0.7eV and one at ~0.65eV. This conclusion is based on the existence of the shoulder at ~0.7eV, seen in data from many different samples.

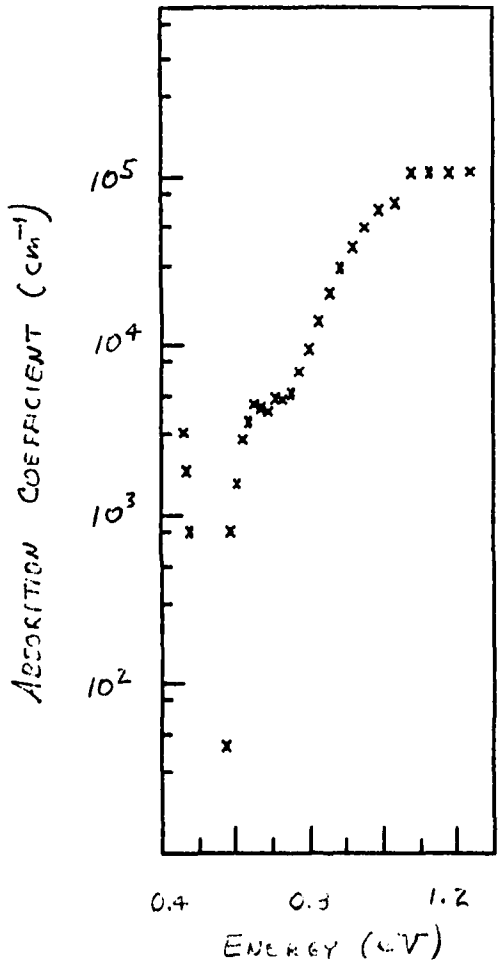
The existence of a direct energy gap is desirable for optoelectronic device development. Further information on transport and photoelectronic properties of $FeSi_2$ layers and $FeSi_2$/silicon heterojunctions is needed to provide a more complete assessment.

Semiconducting $CrSi_2$ films have also been fabricated, indicating an optical absorption edge around ~0.3eV, which is basically consistent with previous transport property studies on this material.

Our initial investigations of these two semiconducting silicide phases were initiated only in the last few months of the contract period. They were undertaken with the intention of broadening our understanding of electronic transport in the transition metal silicides as a class of materials.


REFLECTANCE (PERCENT)
60
50
40
90
70
50
30
10
TRANSMITTANCE (PERCENT)
0
0.2
0.4
0.6
0.8
1.0
1.2
ENERGY (eV)

(a)


ABSORPTION COEFFICIENT (cm⁻¹)
10⁵
10⁴
10³
10²
0.4
0.8
1.2
ENERGY (eV)

(b)

Figure 8.

IV. List of Journal Articles and Conference Presentations

A. Articles:

V. Malhotra, T.L. Martin, and J.E. Mahan, "Electronic Transport Properties of $TiSi_2$ Thin Films," J. Vac. Sci. Tech. B 2(1), 10 (1984).

T.L. Martin, V. Malhotra, and J.E. Mahan, "Electronic Transport Properties of Tungsten Silicide Thin Films," J. Electronic Mat. 13(2), 309 (1984).

V. Malhotra, T.L. Martin, M.T.Huang, and J.E. Mahan, "Summary Abstract: Electronic Transport Properties of Refractory Metal Disilicides," J. Vac. Sci. Tech A 2(2), 271 (1984).

W.A. Metz, J.E. Mahan, V. Malhotra, and T.L. Martin, "Electrical Properties of Selectively Deposited Tungsten Thin Films," Appl. Phys. Lett. 44(12), 1139 (1984).

M.T. Huang, T.L. Martin, V. Malhotra, and J.E. Mahan, "Electronic Transport Properties of Tantalum Disilicide Thin Films," submitted to J. Vac. Sci. Tech. (7/84).

M.C. Bost and J.E. Mahan, "Optical Properties of Semiconducting Iron Disilicide Thin Films," in writing.

B. Presentations:

T.L. Martin, V. Malhotra, and J.E. Mahan, "Electronic Transport and Microstructure in Refractory Metal Silicide Thin Films," 1982 Electronic Materials Conference, Fort Collins, CO (June 23-25, 1982).

T.L. Martin, V. Malhotra, and J.E. Mahan, "Electronic Transport Properties of Refractory Metal Silicides," 30th Nat. AVS Symp., Boston, MA (Nov. 1-4, 1983).

M.T. Huang, T.L. Martin, V. Malhotra, and J.E.Mahan, "Electronic Transport Properties of Tantalum and Molybdenum Silicide Thin Films," 1984 Annual Symp. of the Rocky Mt. Chap. of the AVS, Denver, CO (May 10, 1984).

M.C. Bost and J.E. Mahan, "Semiconducting Chromium Disilicide and Iron Disilicide Thin Films," 1984 Annual Symp. of the Rocky Mt. Chap. of the AVS, Denver, CO (May 10, 1984).

V. Scientific Personnel

A. Principal Investigator:

J.E. Mahan

B. Graduate Research Assistants:

V. Malhotra, M.S. in Electrical Engineering (Dec., 1983)

T.L. Martin, MSEE thesis in writing now

M.T. Huang, MSEE thesis in writing now

M.C. Bost, Ph.D. thesis in progress

ND